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The Vapor Pressure of Aqueous Solutions

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THE VAPOR PRESSURE OF AQUEOUS SOLUTIONS

BY THE AIR BUBBLING METHOD

BY

DAVID KLEIN

THESIS

FOR

DEGREE OF BACHELOR OF ARTS

IN

CHEMISTRY

IN THE

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OF THE

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THIS IS TO CERTIFY THAT THE THESIS PREPARED UNDER MY SUPERVISION# BY

David Klein

ENTITLED The Vapor Pressure of Aqueous Solutions

By the Air Bubbling Method,

IS APPROVED BY ME AS FULFILLING THIS PART OF THE REQUIREMENTS FOR THE DEGREE

OF Bachelor of Arts.

H. N. Parr

HEAD OF DEPARTMENT OF Chemistry.

- The work of this thesis was done under the immediate direction of Professor A. T. Lincoln.

88010

HISTORICAL. The great experimental difficulties attending the direct measurement of vapor pressures have prevented a more extensive knowledge of the vapor pressure of solutions. In fact, most text books on Physical Chemistry state that there are no suitable, practical methods for the direct measurement of the vapor tension lowering. Chronologically, the first method used, commonly known as the "static" method, consists in measuring the depression of the mercury of a Torricellian vacuum, kept at constant temperature, due to the vapor pressure of a solution placed in the barometer tube. By comparing this, with a similar tube, not containing liquid, the vapor pressure lowering at that temperature can be obtained directly. Moser[1], Magnus[2], Wullner[3], Raoult[4], and many others have collected considerable data by this method. Apparently, this is a simple accurate method, yet the researches of Tammann[5] have shown that small quantities of air and impurities greatly influence the vapor pressure. Then too, one cannot be certain that the liquid in the barometer is of uniform concentration, a condition that must be obtained in reliable work. Small drops of solution collecting on the sides of the tube cause a decrease in the vapor pressure, introducing an appreciable error.

An indirect method has found much favor with chemists. This consists in reading the temperature of the boiling solution under various pressures, and as perfected by Ramsay and Young[6], it seems to give good results. Emden[7], etc., have used it to measure the vapor pressure of many aqueous solutions of different concentrations. But this method is not free from serious errors among which may be mentioned the following:- (1) the super-heating of the liquid and vapor; (2) the change in the concentration of the boiling solution due to partial vaporization of the solvent; (3) the great change in the

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boiling point due to a small change in the pressure; (4) it can only be applied to boiling solutions, rendering it useless for many substances which are decomposed by heat. And it might even be suggested that there is something wrong with the method as a means of measuring the vapor pressure of pure water, since no data has been furnished on the subject below 100° C, not even by Ramsay and Young who made the measurements at those higher temperatures. It is desirable that such data be collected, as our present accepted values are by no means correct. Many differential methods have been devised, such as Deterici's[8]. But all the methods mentioned thus far, the "static", Ramsay and Young's "dynamic" and the others have this serious defect, they are too inflexible. In the "static" method, given the temperature, the depression is independent of the volume of solution used; in the Ramsay - Young method given the pressure, the temperature of the boiling solution is determined, independent of the amount of boiling liquid.

It is obvious that a more desirable method would be one whereby the accuracy of the vapor pressure measurements depends upon a condition easily varied by the experimenter. Such a method has been known for a long time, and was employed by Regnault[9] in 1845 when he performed his classic work on the vapor pressure of water. The method is based on Dalton's law of partial pressures, i. e., in a gaseous mixture, under constant pressure, the total pressure is equal to the sum of the partial pressures of the gaseous constituents In a given volume of a mixture of air saturated with water vapor, we would havethis relation, -

$$\frac{\text{the total volume}}{\text{the volume of water vapor}} - = \frac{\text{the total pressure}}{\text{the vapor pressure of water.}}$$

Hence, knowing the total volume, the total pressure, and the volume occupied by the water vapor, the vapor pressure of water could be calculated. The method used by Regnault is as follows:- air was passed through moistened sponge, then through moistened silk cloth fastened on a screen; through absorption tubes into an aspirator of known volume. The experiments were performed in a cave, where the temperature was quite constant. From the data, Regnault calculated the vapor pressure of water at various temperatures and found that they agreed quite closely with his values obtained by the static method. The results appearing in his paper have since been shown to be wrong by Tammann,[10] who has recalculated them and found more divergent results. At the same time, Tammann employed this same method for determining the vapor pressures of solutions and hydrated salts. For the former, his results agree fairly well with other work.

Walker,[11] at Ostwald's suggestion, employed this method, slightly modified, for the determination of molecular weights of substances in aqueous solution. A very slow current of purified air was drawn through a Liebig bulb containing the solution ~~the solution~~; then through a similar bulb filled with pure water, and lastly through an absorption train, filled with pumice moistened with sulphuric acid. The apparatus was placed in a water thermostat; since temperature changes affected the vapor pressure of the solution and water alike, there was no need of keeping the temperature very constant. The loss in weight of the second bulb divided by the gain in weight of the absorption tubes gave directly the relative lowering of the vapor pressure $\frac{f - f'}{f}$, from which the molecular weight of the solute could be calculated. The results were fairly satisfactory. Will and Bredig[12] complicated matters when they introduced a nine

bulb Liebig bulb instead of the usual three-bulb arrangement, in their study of non-aqueous solutions. Orndorff and Carrell[13] have attempted to simplify the method in order to make it suitable for ordinary laboratory practice. Alcoholic solutions of urethane, diphenylamine, nitrobenzene, etc., were used with no distinct success. In his study of hygrometic methods, Shaw[14] devotes considerable space to this saturation method. Regnault's experiments were repeated by him in order to examine the errors at various steps of procedure. The results were about one per cent less than the accepted values for water as given by Regnault; it was found that long rubber connections must be avoided; that glass tubes may be used without any danger of condensation of the water in the saturated air provided these tubes were maintained about one degree above the saturation temperature. Perman[15] has applied this method for the determination of the vapor tension of water and ammonia solutions. He worked carefully and obtained results about one per cent higher than Regnault's tabulated values. Then Carveth and Fowler[16] published an account of their failures to use the saturation method successfully, and also cast doubt upon the accuracy of all former work along this line. They combat Perman's statement "that when air is aspirated through water, it becomes saturated with aqueous vapor with great rapidity,"- not from experimental data but simply by using that dangerous and subtile method- analogy. It is a well know fact that some solutions become saturated with salts with great difficulty; and from this they argue that gases ought to become saturated with aqueous vapor only with great difficulty. They then raise the question- "Is the same result obtained when treating a gas with water vapor to saturation as when bringing the gas from a condition of super-saturation to saturation, and have all results obtained hitherto been obtained from gases not

Figure I.
The Saturator.

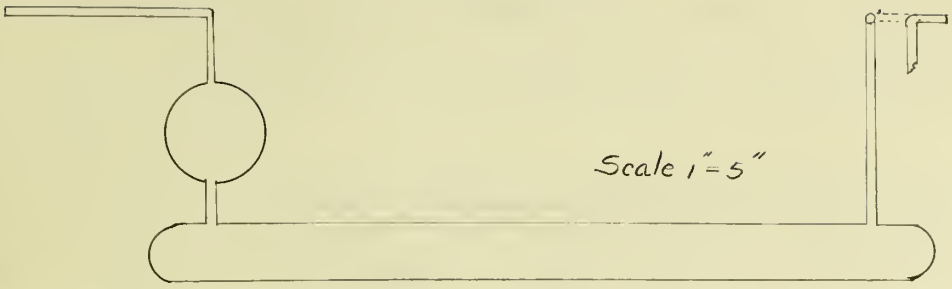
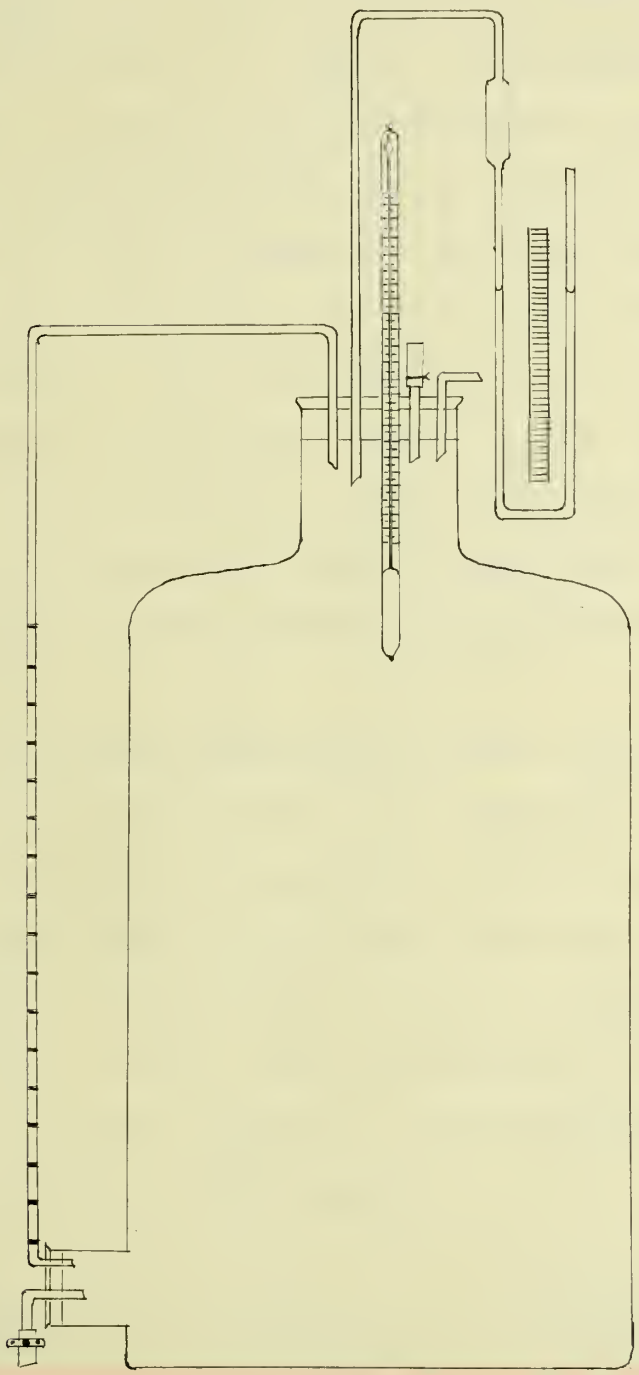


Figure III
Aspirator.

Scale 1"=5".



completely saturated"? The experiments of Carveth and Fowler are too few and unsatisfactory to throw any light on the question, and indeed their condemnation of the method may be ascribed to experimental difficulties.

The saturation method possesses many advantages over the other methods in that (1) measurements may be made at ordinary temperatures and pressures, in a comparatively short time; (2) that no chemical decompositions occur in solutions, such as are known to occur in boiling liquids; (3) that no costly apparatus is involved. But as employed by Walker, Will and Bredig and others, the method has grave objections among which may be mentioned the following:- (1) the pressure is not the same in the bulbs containing the solvent and the solutions, and as the difference may be very considerable, the error introduced is not negligible; (2) it is well known that the concentration of the surface layers of the solution differs from the concentration of the rest of the liquid; and as these surface layers are the last ones with which the air comes in contact, the true vapor pressure of the solutions are not being measured.

EXPERIMENTAL.-

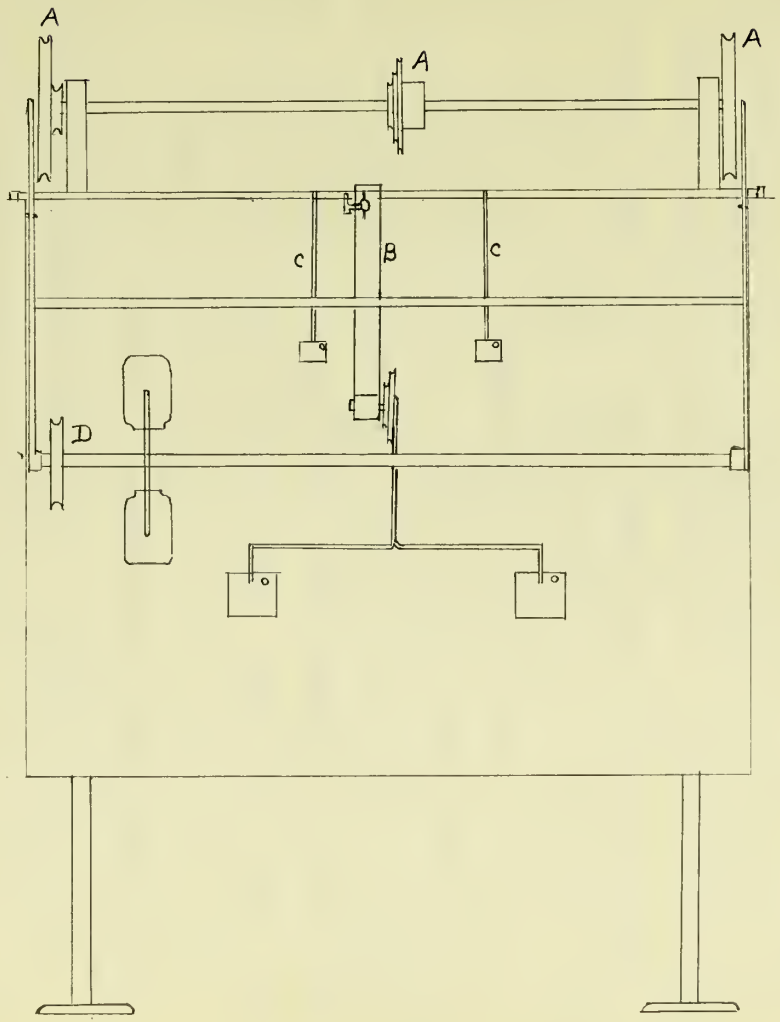
It therefore seemed advisable to study the limitations of this saturation method and to perfect the apparatus to obviate some of the difficulties hitherto encountered. At the suggestion of Prof. Kahlenberg of Wisconsin the following method was employed. Instead of passing the air through bulbs filled with liquid kept motionless, the air was drawn through a tube continually in motion, so that the contents were violently agitated. The parts of the apparatus employed are described in some detail.

THE SATURATOR.-

The liquid whose vapor pressure was to be measured was placed

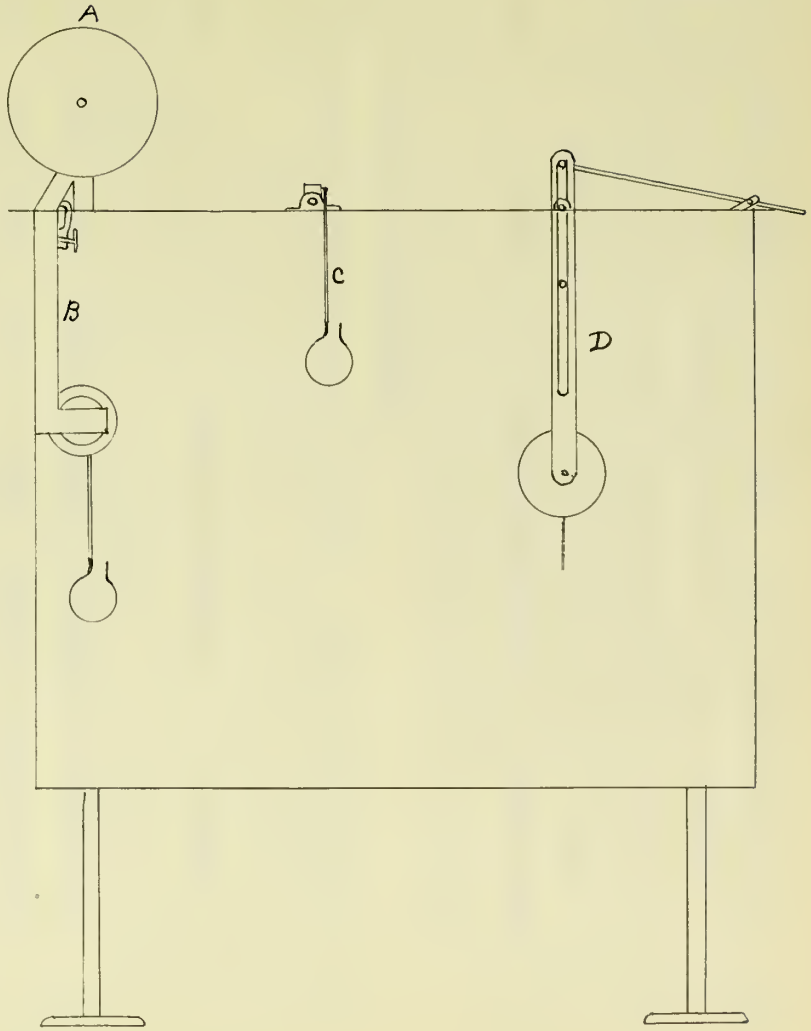
Figure II

End View



Side View.

Scale 1" = 8"



in the glass vessel shown in Fig. one. This "saturator" was made entirely of glass, of the dimensions given in the diagram. The small bulb prevented liquid particles from being carried over mechanically. The tube C was filled half full of the liquid, about 150 cc., and then placed in a thermostat where it was connected with a shaking device to keep the solution continually in motion.

THERMOSTAT AND SHAKING APPARATUS:-

The thermostat consisted of a large, square galvanized tank 30" x 30" x 25". The thermo-regulator was of the ordianry toluene-mercury type, and it was by no means difficult to maintain the temperature within ±.02°C as read on a Beckmann's thermometer. After many unsuccessful trials with various kinds of shaking apparatus, the following was constructed, and it gave complete satisfaction. Along the upper edge of one side of the thermostat was fastened an axle bearing at each end a heavy cast iron pulley 6" in diameter. Upon this same axle was a cone pulley of three cast iron pulleys (2" - 3" - 4"). Directly beneath this pulley was a similar brass pulley, fastened to a heavy cast iron block, which was held in position in the tank by a clamp. On this lower pulley was an eccentric shaft, forked at the free end and terminating in two brass collars, so arranged as to fit the glass saturator and then they could be tightened by a nut and bolt arrangement. Across the top of the tank, a
9 1/2" from the side bearing the pulleys, was placed a wooden strip, from which were hung two heavy copper wires, their free ends terminating in two collars, similar to those on the eccentric shaft. These were also fastened around the saturator and served to keep the tube at the proper depth in the bath. Lastly, the tubes A and D (fig.1) were bound by means of copper wire to the wooden strip, a little free play being permitted. A stirring device to keep the

water of the thermostat in circulation is also shown in fig.2, with the rest of the device. The stirrer consisted of a pulley and axle, bearing a large brass paddle. One of the large iron pulleys before mentioned was belted to a 1/6 H.P 100 volts direct current motor 1600 R.P.M., giving the saturator a speed of about 200 R. P. M. with a 1" stroke.

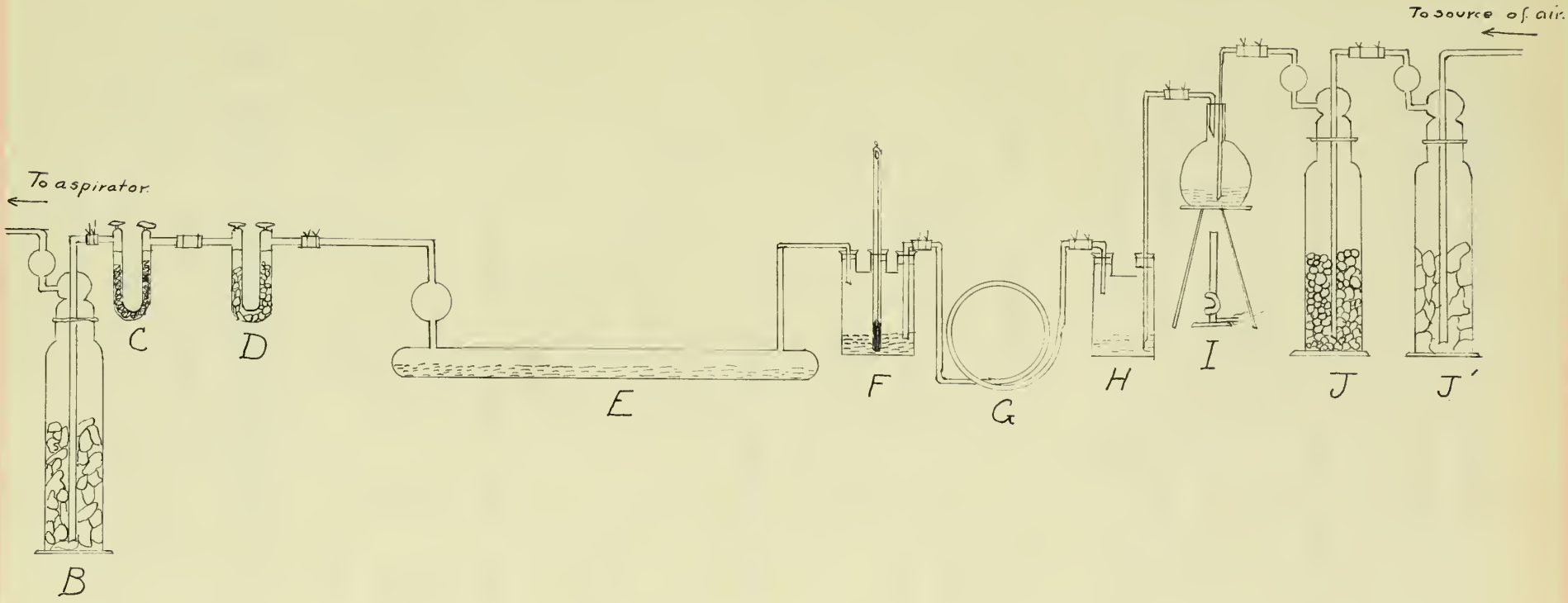
ASPIRATORS:-

The aspirators used were made of glass, each of 32 liters capacity. The arrangement of the aspirators is shown in fig.3. The mouth of the bottle was tightly closed by means of a large rubber stopper, containing 5 holes, to admit the following:- a calibrated thermometer, graduated to tenths, and estimated to hundredths; an open oil manometer; a bent tube to connect the aspirator with the rest of the apparatus; a small tube, to permit of air exit when the aspirator was being filled, and which was closed by a screw cock when the aspirator was filled; and also a tube from the glass water-level, the lower end of which was fastened in the lower stopper. This water-level was used as an indicator of the amount of water that had been aspirated and consequently, it had to be calibrated very accurately. The calibration of the aspirators was accomplished by allowing the contents of the bottle to run into carefully graduated two-liter flasks, and marking the height of each two liters on the water level. This operation was repeated several times and verified by weighing the aspirators when filled with water and also when empty, a Fairbank's scale accurate to 0.002 lbs., being used to weigh the aspirators. A comparison of the following data shows that the volume of the aspirators was known quite accurately. The aspirators are A and B.

	A	B
By direct calibration	24.0	32.0

Figure IV

Scale 1" = 8"



8) By weighing 23.98 31.96

The drying train consisted of two tubes with ground glass perforated stoppers of the Schwartz type; one containing pumice moistened with sulphuric acid; and the other filled with alternate layers of glass wool and phosphorus-pentoxide. After each experiment, the sulphuric acid was decanted from the pumice, the tube rinsed out with fresh sulphuric acid and then a very small quantity of fresh acid was poured in, not enough to fill the lower part of the U tube. The phosphorous pentoxide tube served for many experiments without refilling.

Fig.4, is a diagramatic representation of the apparatus, as employed in most of the experiments. The air was drawn from out-of doors, passed through the Drechsel wash bottles J and J', the latter containing pumice moistened with sulphuric acid, the former filled with soda lime; these bottles were used to free the air of ammonia and carbon-dioxide. Next, the air bubbled through pure water (I) maintained at a high temperature. We shall call this the "supersaturator", where the air becomes saturated with more water vapor than it contains at 25°C; in other words, it is supersaturated as far as the temperature of the experiments is concerned. The Woulff bottle H, placed in the thermostat, contains pure water to bring the air to saturation at 25°C. In order to aid this condensation, the lead coil G, about 5' long is placed in the bath, and by the time the air reaches F, it is cooled to 25°C. F is another Woulff bottle in the bath, containing a solution of the same strength as that in the saturator; this served to bring the air down to the saturation point of the solution, so that there would be little change in the concentration of the solution in the saturator. After passing through the saturator E and the absorption tubes D and C, the air was stored in the aspirator A; the washbottle B containing pumice and sulphuric acid, preventing any moisture from passing from

the aspirators into the absorption tubes.

Throughout this work, the greatest care was taken to have all the apparatus and water free from fatty or oily matter. All the glass parts were cleaned with potassium bichromate and sulphuric acid, and then steamed out with fat free water. This water was also used in making the solutions. Ordinary distilled water was distilled from permanganate and sulphuric acid into barium hydrate, from which the pure water was slowly distilled.

Another precaution that was considered necessary was that the horizontal outlet tube of the saturator must be perfectly clean and dry. If any of the salt should remain in this tube, a slight amount of it would dissolve in the aqueous vapor, be carried into the absorption tubes and vitiate the results. Moreover, in the case of salts that form hydrates, they would abstract water from the saturated air, and too little water would be absorbed by the pumice. Since this horizontal tube projected out of the bath, and as the room temperature was usually lower than that of the saturated air, it was necessary to heat this tube above the temperature of the bath to prevent condensation of the water vapor. This was only necessary in the case of pure water and dilute solutions, since in the case of concentrated solutions the amount of water contained in the air was far below the saturation quantity. The heating was easily supplied by passing an electric current through a platinum wire coiled around the tube.

The calculations in all the work have been made by means of the following formula given by Tammann:-

$$f = \frac{H}{1 + \frac{V\,(1+K\,t')\,W\,d\,(H-f')}{P\,(1+K'\,t')\,760}}$$

where t - temp. of the saturated air.

where f - vapor pressure of water vapor at t.

t' - temp. of aspirator at the end of an experiment.

f' - vapor pressure of water at t' (found in L-B tables)

H - barometer reading corrected to 0^{o}.

K' - coefficient of expansion of air - 0.003671

K - " " " " water (negligible)

V - volume of aspirator at 0 C.

W - absolute weight of 1 liter of air at o^{o} C.

d - theoretical density of water vapor.

Wd - .8042 grams.

P - weight of water absorbed by absorption tubes.

The first experiments were intended to settle some of the disputed points of this method and also to note the limitations and efficiency of the apparatus. At once the following questions arose for settlement:-

(1) Does the rate of aspiration have any effect on the vapor pressure? (2) Is the air saturated and how can it be shown that equilibrium exists between the air and water? Now as regards the first question, Regnault[9] found that the rate of aspiration had no effect on the vapor pressure of water, even when the rate was about 25 liters an hour. This conclusion was also arrived at by Tammann,[10] who drew the air through the apparatus at the rate of 6 to 10 liters an hour. Yet more recent workers have deemed such rates far too high for accurate results. Ostwald and his followers in this work rarely exceeded three to four liters per hour, and in most cases the flow was less than this. "It is of interest to note that Tammann found that the time required in the passage of a definite volume of air had no effect on the results - a deduction which must, if care be not taken to define the conditions more exactly, lead to an

Table I.

The influence of the rate of aspiration on the vapor pressure.

H	V	t'	rate in liters per hr.	H - f'	P	f
733·70	28	21·00	5	715·20	·6608	23·84
734·48	32	23·05	5	713·58	·7434	23·72
741·60	32	22·20	8	721·70	·7506	23·84
748·94	32	20·85	10	730·61	·7549	23·78
753·25	32	23·98	16	731·10	·7411	23·76

Table II.

Vapor pressure of water - without supersaturation.

H	V	t'	H - f'	P	f
740·53	26	23·30	719·27	·6060	23·83
749·61	32	22·50	729 47	·7456	23·71
733·70	28	21·00	715·20	·6608	23·84·
728·21	32	22·80	707 58	·7451	23·75
752·36	32	20·60	734·30	7506	23·67
747·92	32	21·70	728·61	·7467	23·67
734·48	32	23·05	713·58	·7434	23·72
743·40	32	20·60	725·34	·7504·	23·65
741·81	32	23·90	719·76	·7420	23·74
750·51	32	19·75	733·32	·7580	23·80
741·60	32	22·20	721·70	·7506	23·84
739·72	32	17·30	725·00	·7690	23·84
				Mean	23·755

Table III

Vapor pressure of water - with supersaturation.

H	V	t'	H - f'	P	f
748·94	32	20·85	730·61	·7549	23·78
754·16	32	21·88	734·64	·7493	23·76
753·25	32	23·98	731·10	·7411	23·76
				Mean.	23·76

absolute absurdity". This quotation is from Carveth and Fowler, and as my experiments show the "absolute absurdity" is more on the side of the above quoted authors, who aspirated the air "rather rapidly" at the rate of 3/4 liter per hour! Table I gives the results of the effect of the rate of flow on the vapor pressure of water. It is readily seen that the vapor pressure is independent of the rate of aspiration, even when the rate was changed three-fold. The rate of 16 liters per hour is by no means the limit speed, for subsequent experiments were made with much faster flow. This then would give at least one proof that the air is saturated, or else how could it be explained that the vapor pressure remains constant under such diverse conditions? But a more conclusive proof is given below.

PROOF OF SATURATION OF AIR.-

Carveth and Fowler have raised the question that all previous work has been done with non-saturated air; that results will be different if the air is brought to a state of saturation from non-saturation than if air super-saturated with water vapor is brought to a state of ~~super~~-saturation by passing the air through water. This seemed obviously incorrect and the following experiments were made to settle the question. The wash bottles H and I were removed, and the unsaturated air was passed directly into G. With this arrangement, vapor pressure determinations of pure water were made as in the case of those in T able I; the results being embodied in Table II. Then the wash bottles H. and I were replaced, the temperature of I raised to 50° - 60°, and experiments similar to those in Table II were made, and the results are given in Table III. It will be seen that the results are identical in the two cases of super-

saturation and under-saturation; equilibruim has been approached from both sides, proving conclusively that the air is saturated, and contradicting Carveth and Fowler's conclusion that " it is easy to obtain conditions of super-saturation which are not readily displaced to equilibrium by the presence of an excess of the solute phase".

In measuring the volume of air drawn through the apparatus, it has always been tacitly supposed that the air in the aspirator is saturated with water vapor, and hence the correction for the observed temperature was the one found in Regnault's table. Even Shaw in his careful work states, "that we may assume that the air in the aspirator is saturated". To verify this assumption, the following experiment was performed:-

At the close of a determination of the vapor pressure of water, the pressure and temperature of the air in the aspirator were noted. The aspirator was then tightly closed to prevent any leakage and allowed to remain until the next morning, when its pressure and temperature were again noted. A few hours later, the same readings were taken, and from this data, assuming the air saturated the true volume of the air in the aspirator was calcualted. The results were

Volume	Time
1.---21.15 l.	0 hours
2.---21.14 l.	12 "
3.---21.18 l.	15 "

It therefore seems that the assumption made above is valid, and was used throughout these experiments.

To preclude any objections that might be raised to the effect that particles of solution are carried over mechanically, the following experiment was performed with a Lithium Nitrate solution in the saturator. Instead of passing the saturated air through the

Table IV

Vapor pressure of potassium nitrate solutions.

C.	H	V	t'	H - f'	P	f''	$\mu = \frac{f - f''}{f c} 1000$	M
2177	738·45	32	20·75	720·22	·7063	22 33		
"	752·09	32	24·50	729·24	·6977	22 47		
"	753·44	32	24·30	730·86	·7006	22·53		
"	752 05	32	24·60	729 06	·6976	22·47		
"	744·08	32	24·50	721·33	6947	22·57		
"					Mean	22·49	2·46	69·39
1045	746·26	32	24·00	724·08	·7196	23·09		
"	743·04	30	22·00	723·38	·6843	23·19		
"	745·17	28	21·30	726·33	·6361	23·01		
"	750·38	32	22 10	730·60	· 7237	23·00		
"	750·89	32	21·90	731·35	·7271	23·08		
"	745·28	32	22·90	724·52	·7267	23·18		
"					Mean	23·09	2·70	64·83

Table VI

Vapor pressure of sodium nitrate solutions.

C.	H	V	t'	H - f'	P	f''	$\mu = \frac{f - f''}{f c} 1000$	M
7565	740·75	32	29·50	710·09	·5572	18 55		
"	741·46	32	27·60	714·01	·5633	18·55		
"	740·82	32	28·75	711·47	·5613	18·51		
"					Mean.	18·54	2·92	48·13
4953	739·09	32	28·55	71008	·6060	20 02		
"	740·04	32	27·85	712·19	·6103	20·08		
"					Mean	20·05	3·15	48·18
3248	741·08	32	23·90	719·03	·6601	21·22		
"	740·18	32	24·02	718·00	·6588	21·20		
"					Mean	21·21	3·31	48·63
1169	736·41	32	24·95	712·93	·7052	22·76		
"	735·67	32	24·75	712·48	·7074	22·80		
"					Mean.	22·78	3·53	48·91

absorption tubes, it was made to pass through an empty U tube, placed in ice water. The liquid thus collected gave no test for lithium or for nitrates, proving the efficacy of the small bulb on the saturator.

Being convinced that the method was thoroughly reliable I next turned my attention to the study of solutions, beginning with very concentrated ones, and diluting them. The method was essentially the same as in the case of pure water; the solution was placed in the saturator E and the Woulff bottle F. C contained pure water to produce equilibrium from the "supersaturator" I. In most cases it was not necessary to raise the temperature in I above that of the room, since the vapor pressure of the solution was much less than that of water.

Potassium Nitrate was the first substance studied. The salt, recrystallized Kahlbaum's preparation, was dissolved in pure water and the contents analyzed as follows:- A portion of the solution was drawn into a fine - bore 10c.c. pipette, the large end of which could be closed by means of a rubber tube and screw-cock. After the filled pipette was weighed the contents were run into a weighed platinum dish and evaporated to dryness. The residue was heated in an air-bath at 110° C. to constant weight. Duplicate samples gave very concordant results. After a sufficient number of determinations were made, so that the vapor pressure of the solution was known quite accurately, the solution was diluted and the rest of the procedure is as above. Table IV gives the results for the solutions. In this and subsequent tables, the concentration is always expressed in the number of grams of solute in one hundred grams of water. To demonstrate that no appreciable changes of concentration occur in the saturator, analysis of the saturator solution was made after the the termination of the measurements recorded in Table IV. The results

Table V.

Vapor pressure of lithium nitrate solutions.

C	H	V	t'	H-f'	P	f''	$\mu = \frac{f-f''}{fc}1000$	M
57.18	747.06	32	22.90	726.30	.4649	15.00		
"	746.26	32	21.40	727.30	.4662	14.93		
"	744.02	32	22.60	723.66	.4645	14.97		
"					Mean	14.97	6.47	17.53
47.86	734.44	32	22.60	714.05	.5216	16.76		
"	741.37	24	23.30	720.11	.3858	16.64		
"	739.86	32	27.00	713.28	.4995	16.83		
"					Mean	16.74	6.18	20.54
40.21	749.82	32	22.60	729.43	.5509	17.69		
"	748.12	32	24.45	725.33	.5464	17.71		
"	748.00	32	24.68	725.90	.5451	17.67		
"					Mean	17.69	6.36	21.09
31.82	741.53	32	26.10	716.39	.5823	19.01		
"	738.57	32	25.55	714.24	.5852	19.05		
"					Mean	19.03	6.25	23.04
23.08	742.34	32	22.95	721.52	.6397	20.49		
"	741.98	32	22.40	721.84	.6410	20.45		
"	734.41	32	23.05	713.47	.6391	20.48		
"					Mean	20.47	6.01	25.85
16.82	742.36	30	24.80	719.09	.6216	21.42		
"	741.09	32	24.70	717.96	.6653	21.48		
"	734.86	32	26.00	709.87	.6613	21.49		
"					Mean	21.46	5.73	28.25
11.61	730.29	32	23.05	709.34	.6931	22.17		
"	728.43	32	23.18	707.35	.6923	22.16		
"					Mean	22.17	5.79	28.94
8.41	740.52	32	24.25	718.10	.7068	22.72		
"	740.92	32	23.30	719.66	.7078	22.65		
"	740.55	32	21.10	721.93	.7170	22.69		
"					Mean	22.69	5.35	32.40
5.14	745.26	32	22.05	725.54	.7298	23.19		
"	742.65	32	22.95	721.77	.7268	23.19		
"	742.65	32	22.00	723.02	.7286	23.15		
"					Mean.	23.18	4.75	36.98

are as follows:-

Before experiments were made	9.45%	KNO_3
	9.46%	
After " " "	9.46%	
	9.46%	

It is therefore possible to avoid concentration changes in the saturator, by passing the air through a sufficient number of Woulff bottles containing the solution, before it reaches the saturator.

Because of its great solubility, Lithuim Nitrate was next selected as suitable for the measurement of the vapor pressure of concentrated solutions. The salt was recrystallized several times, and dissolved in pure water. For analysis, samples of the solution were weighed out as in the case of KNO_3, evaporated to dryness, moistened with H_2SO_4 and after carefully driving off the excess of acid, weighed as Li_2SO_4. After a little experience it was possible to obtain very satisfactory duplicates. After the vapor pressure was determined at any concentration, the solution was diluted and the measurements repeated. Table V embodies the results obtained over quite a range of concentrations.

A similar set of data was obtained for sodium nitrate, given in Table VI. The salt was furnished by Prof. Kahlenberg; and it proved to be a very pure product of Kahlbaum. Analysis of the solution was made by evaporating a portion of it to dryness, and after drying at 115 °C. weighed as the nitrate.

DISCUSSION:-

It will be seen that the value for the vapor pressure of water given above is somewhat higher than Regnault's value for 25°C- 23.55. This result was unexpected as previous workers with the same method have found that the values obtained were about one per cent less than the values of Regnault. It is interesting to note that Perman's

results fully agree with mine, since his values for 20 and 30° C were also higher than the tabulated values by about one per cent. In fact, the accuracy of Regnault's values might be questioned, since the experimental data does not permit of the numerous recalculations and corrections that have been made. New determinations of the vapor pressures of water would be of much value, and the air-bubbling method is quite suitable for such experiments, since the experimental errors could be greatly reduced by aspirating large quantities of air. In that case, however, the air would have to be collected over some substance other than water, whose vapor pressure was accurately known.

In tables IV -VI, the columns headed μ represent 1000 times the relative lowering which one gram of substance would produce at a particular concnetration. According to Wüllmer's law, the value for μ should remain constant. In terms of the dissociation theory, μ should decrease with increasing concentration. In the case KNO_3, μ decreases with increasing concentration, quite in accord with the results of others, as table VII clearly shows.

Table VII.

Con.	μ		
25.04	2.52	100° C.	Determined by
11.76	2.75		Tammann
11.222	2.87	18°-20°	Walker
20.071	2.38	25.86°	Emden
10.036	3.00		

But for $LiNO_3$ the results are quite different. The values for μ increase with increasing concentration, in a very noticeable manner. If then the vapor pressure lowering depends upon the number of molecules in sclution, the above facts indicate that there are relatively more particles dissociated in a strong $LiNO_3$ solution than

in a dilute one. Tammann's results indicate the same thing as the following table shows:-

Table VIII.

	$LiNO_3$		
	Con.		
T.	15.92	35.01	59.06
	μ	μ	μ
30.9	7.57	7.40	6.63
38.2	6.56	7.11	6.87
46.7	5.71	6.29	6.46
50.4	5.61	6.25	6.44

For $NaNO_3$ μ decreases with increasing concentration, as in the case of KNO_3 . There are however many discrepancies between the values of μ as found above and those obtained by other workers.

Another very striking fact is the great variation in the value of μ, for the different salts. If the vapor pressure lowering simply depends upon the number of molecules in solution, why does $LiNO_3$, conc. 11.61, lower the vapor pressure twice as much as a solution of KNO_3, conc. 10.46, and over one and one half times as much as a solution of $NaNO_3$, conc. 11.69? It may be answered that $LiNO_3$ is more dissociated than KNO_3 or $NaNO_3$. If that is so, then the "abnormality" of the molecule weight of $LiNO_3$ should be relatively greater than for either KNO_3 or $NaNO_3$. Raoult has shown experimentally and Van't Hoff mathematically that it is possible to calculate the molecular weight from the vapor pressure measurements as follows:-

$M = \frac{18\ c\ f'}{f - f'}$, where 18 is the molecular weight of water, c, f and f' having the same significance as before.

Kahlenberg[18] found the molecular weight of KNO_3 by the boiling point method to be 65.0 at a cone of 21.333 grams, and 61.5 at a conc.

of 9.727 grams. Jones - Barnes - Hyde[19] give the value 70.9 for the molecular weight of KNO_3, conc. 10.119 grams, by the freezing point method. It is therefore evident that the values obtained by the vapor pressure method agree equally well with those obtained by the "standard methods".

Applying the same formula to $LiNO_3$, we find the surprising value of 17.53, in the most concentrated solution whereas the theoretical molecular weight is 69.07. Only in a solution of 5.14 grs. per 100 does the molecular weight come within one-half of the weight corresponding to the formula $LiNO_3$. In other words $LiNO_3$ dissociates into more than two ions, even in fairly dilute solutions; an obviously absurd conclusion. More than this, the calculated molecular weight decreases with increasing concnetration; also contrary to the dissociation theory. It is more dissociated in a solution containing 57.18 grams per 100 of H_2O, than in a solution containing 5.14 grams per 100 of H_2O. It might be asserted that the measurements and hence the molecular weights are very wrong. In that case, the freezing point determinations of Biltz[20] are very wrong, since he found that the molecular weight of $LiNO_3$ · solution of 7.02 grams per 100 H_2O is 36.8, while in a solution of 1.154 grams per 100 H_2O, it is 38.4!

The molecular weights for $NaNO_3$ remain very nearly constant over quite a range of concentrations, and are nearly one-half the theoretical molecular weight. The explanation of this is not apparent at present.

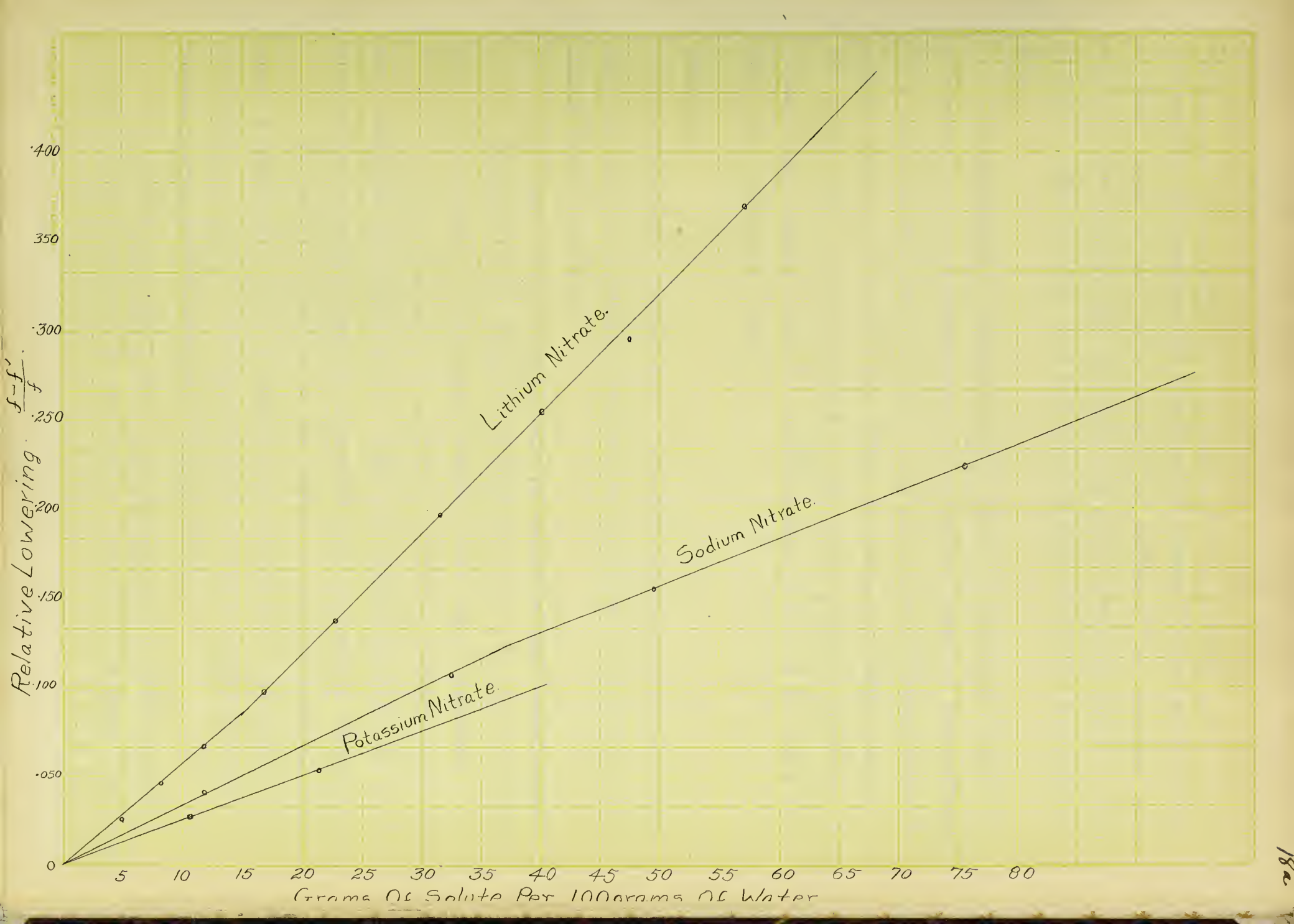
However, it might be argued that Raoult's formula does not apply to very concentrated solutions. To be sure, as originally promulgated it was only an approximate formula. But it is employed to calculate molecular weights in dilute solutions, and where are

we to draw the line between dilute and concentrated solutions?

It is again coming to be recognized that there are other factors than the mere number of particles in solution that influence the depression of the vapor tension and of the freezing point and also the rise of the boiling point. Chemical affinity, here comes into play, and there is some reaction between all the solvent and all the solute. It is interesting to note in this connection that Dr. Nicol[21] held similar views in 1886 when he said" it may be noted in passing , that unless a salt molecule were capable of disturbing the equilibrium of the whole of the water molecules present, it could have no effect on the vapor pressure of the water". Dr. Kahlenberg[18] says, "We have seen above (and the literature is replete with records of facts illustrating the same point) that substances of similar chemical composition, when dissolved in the same solvents behave similarly, as far as the changes of the boiling or freezing points are concerned; this clearly shows that the influence of the chemical nature of the dissolved substance enters into the determination of the molecular rise of the boiling point - and the molecular lowering of the freezing point". He might equally as well made his remarks apply to the vapor pressure determinations.

The following table, compiled from Tammann's work as given in Landolt-Bornstein's Tabellen, gives the lowering of the vapor pressure of water at 760 mm, caused by approximately the same concentration of various salts of sodium, potassium and lithium.

	Na		K		Li	
	conc.	lowering	conc.	lowering	conc.	lowering
Cl.	36.91	187.5	31.68	108.0	36.6	341.8
Br.	38.98	117.3	32.70	69.8	31.6	124.1
NO_3	37.00	98.4	33.90	64.2	32.5	145.9
I	36.00	77.0	30.70	47.6	34.9	88.5
SO_4	32.89	56.5	21.22	32.1	30.2	81.1


Relative Lowering. $\frac{f-f'}{f}$.
·400
350
·300
·250
·200
·150
·100
·050
0
Lithium Nitrate.
Sodium Nitrate.
Potassium Nitrate.
5 10 15 20 25 30 35 40 45 50 55 60 65 70 75 80
Grams Of Solute Per 100grams Of Water

For each of the metals, the lowering decreases for the acid radical in order given in the table, except for $LiNO_3$. Or for the same acid radical, the lithium salt produces a greater lowering than the sodium salt. This is also true for the nitrates at 25° C, as my data show.

The accompanying curves show the relation existing between the concentration (as abscissas) and the relative lowering (as ordinates) The points lie well upon definite straight lines; although there is a sharp break in the curve for $LiNO_3$; and also for $NaNO_3$. However, in the former case, it would seem that the vapor pressure lowering increases too rapidly with the concentration, while in the case of $NaNO_3$,the reverse is true.

SUMMARY.-

In this paper, it has been shown how certain improvements have made the saturation method the most accurate way of directly determining vapor pressures.

2. We have proved that the air is saturated with water vapor.

3. Regnault's and Tammann's statements that the rate of aspiration has no effect on the vapor pressure have been confirmed.

4. The vapor pressure of solutions of KNO_3 and $NaNO_3$ agree with the dissociation theory;while those for $LiNO_3$ contradict it, in as much as the relative lowering increases with increasing concentration.

5. If Raoult's formula is applicable to concentrated solutions, then the molecular weight of $LiNO_3$ is far below that required by the dissociation theory for complete dissociation. Moreover, these values increase with decreasing concentration.

6. It has been shown that the lowering of the vapor pressure is not solely a function of the number of parts in solution; but that

the specific affinity of each salt must be taken into consideration.

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